BRIEF COMMUNICATIONS

FUROCOUMARINS FROM THE ROOTS OF ANGELICA BREVICAULIS

N. S. Ignat'eva and G. K. Nikonov

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The present communication gives the results of a study of the lactones that we have found in the roots of Angelica brevicaulis (Rup.) (Archangelica brevicaulis (Rchb.)), a perennial herbaceous plant of the family Umbelliferae (collected in the region of Przheval'sk, KirgSSR).

A preliminary study showed that the roots of the plant contained 4.34%, and the fruit 1.58%, of total coumarin derivatives. These consist of mixtures of the same components, with R_f 0.90, 0.80, 0.75, 0.71, 0.60, and 0.03 [in the petroleum ether (bp 40°- 60° C—benzene—methanol (5:4:1) system on paper impregnated with 10% of formamide in methanol]. Absorption chromatography on a column of acidic alumina (activity grade II, 30 × 7.5 cm) and elution with ethyl alcohol gave 26 fractions. We have isolated five individual lactones by rechromatographing the fractions and repeated recrystallization from benzene and methanol. From the elemental analysis, melting point, IR spectrum, and mixed samples, these substances were identified as the furocoumarins pimpinellin, isobergapten, isopimpinellin, bergapten, and sphondin.

Attention is attracted by the peculiar composition of the furocoumarin complex of Angelica brevicaulis, which is distinguished by the simultaneous presence of isomeric pairs of substances of the psoralen and angelicin series: isopimpinellin and pimpinellin, bergapten and isobergapten.

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5-O-DESMETHYLNOBILETIN FROM ASTER ALTAICUS

A. T. Troshchenko and T. I. Limasova

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We have investigated the chemical composition of Aster altaicus Willd. collected in 1963 in the Gornyi-Altai Oblast.

The epigeal part of the plant was extracted with petroleum ether. On standing, the concentrated extract deposited an amorphous brown precipitate which was recrystallized three times from methanol. This gave yellow silky needles with mp 143°-145° C. Yield 0.02% of the air-dry herb. With ferric chloride, the substance gave a green coloration, and it also gave a positive reaction for flavones with zinc dust and hydrochloric acid.

Elemental analysis shows that the substance obtained has the composition $C_{20}H_{20}O_8$ and contained 38.92% of methoxy groups. UV spectrum: λ_{max} 254, 284, 344 mμ (log ε 4.078; 4.461; 426, respectively). The spectrum is characteristic for flavones [1].

The properties of this compound are very similar to those of 5-O-desmethylnobiletin (5-hydroxy-6, 7, 8, 3', 4'-pentamethoxyflavone) [2].

On methylation with dimethyl sulfate for 54 hr, the substance was converted into nobiletin (5, 6, 7, 8, 3', 4'-hexamethoxyflavone) with mp 136°-137° C. Its melting point and UV spectra agreed with literature data [3, 4].

Demethylation of the substance isolated from the plant by means of hydriodic acid gave 5, 6, 7, 8, 3', 4'-hexahydroxyflavone [5].

Methylation of this compound with diazomethane [6] gave 5-O-desmethylnobiletin identical with that obtained from the plant.

We obtained the same 5-O-desmethylnobiletin by treating the nobiletin that we had prepared, with aluminum chloride in ethereal solution at room temperature.

Selective demethylation in position 3 has been recorded for a number of flavones [7]. Veratric acid and acetoveratrone were isolated from the products of the alkaline decomposition of the flavone. The hypsochromic shift observed on methylation is characteristic for flavones having a free hydroxy group in position 5 [6].

The spectra of the substance from the plant and its aluminum complex showed the bathochromic displacement characteristic for them [8]. When the UV spectra taken in an alcoholic solution and in sodium ethoxide solution were compared a characteristic shift was again observed [9].

Thus, we have established the identity of the compound isolated as 5-hydroxy-6, 7, 8, 3', 4'-pentamethoxyflavone (5-O-desmethylnobiletin).

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Novosibirsk Institute of Organic Chemistry,
Siberian Division, AS USSR, Novosibirsk

SYNTHESIS OF A MERCAPTOETHYL ETHER OF DEXTRAN

O. A. Zavada, A. D. Virnik, K. P. Khomyakov, and Z. A. Rogovin

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The synthesis of physiologically active derivatives of dextran is arousing great interest [1–4], particularly derivatives of dextran containing mercapto groups. It is known that low molecular weight compounds including a mercapto group have a favorable action in the treatment of disturbances of the connection between respiration and the formation of adenosine triphosphate [5].

The dextran ether was synthesized by treating dextran with ethylene sulfide. 15 g of dextran was dissolved in 45 ml of 18% caustic soda, precipitated with methanol, dried, and treated, with stirring, with 300 ml of ethylene sulfide at 20° C for 4 hr, after which the precipitate was filtered off, washed with benzene, and dried.

In the reaction of dextran with ethylene sulfide there is the possibility of the simultaneous formation of the mercaptoethyl ether and of a graft copolymer of dextran and poly(ethylene sulfide), while the thiol groups of the alkyl residues and the graft chains may be oxidized in the air with the appearance of disulfide bonds. The product of the reaction contained 32% of sulfur and only 0.2% of thiol groups. Thus, under the conditions for synthesis used the oxidation of the thiol groups of the alkyl residues and the graft chains takes place almost completely.

To reduce the disulfide bonds, the products were treated with 250 ml of 5% hydrosulfite at 20° C for 24 hr. An insoluble copolymer of dextran and poly(ethylene sulfide) containing 38% of sulfur and practically free from thiol groups was separated by filtration. The copolymer was found to contain 30% of dextran and 70% of poly(ethylene sulfide). In view of the fact that in the graft copolymer the thiol groups are present only at the ends of the graft chains, it may be concluded that the molecular weight of the graft chains of the poly(ethylene sulfide) is very high.

The filtrate was acidified with hydrochloric acid, and methanol then precipitated a water-soluble derivative of dextran which was purified by pouring an aqueous solution into methanol. To characterize the composition of the product obtained, the total content of sulfur was found and the electrical exchange capacity was determined by the iodometric method. The product contained 20% of sulfur and the electrical exchange capacity was 6.2 mg-eq/g. At this value of the exchange capacity, the sample should contain 20.4% of thiol groups, i.e. practically all the sulfur atoms should be present as thiol groups, and the sample synthesized was a mercaptoethyl ether of dextran with a γ value of 165, which corresponds to the formula

$$[C_6H_7O_2(OH)_{1.35}(OCH_2CH_2SNa)_{1.65}]_n.$$